



Single layer fuel cell based on a composite of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}-\text{Na}_2\text{CO}_3$ and a mixed ionic and electronic conductor $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$



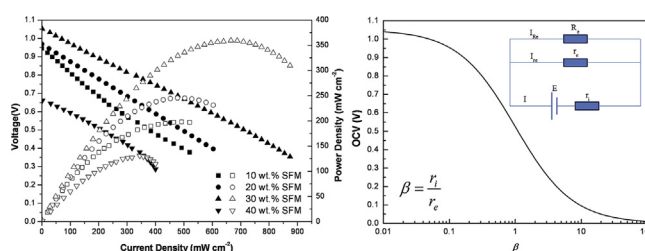
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HIGHLIGHTS

- Single layer fuel cells are fabricated with the mixture of SFM and $\text{SDC}-\text{Na}_2\text{CO}_3$.
- The fuel cell with 30 wt.% SFM gave the highest 1.05 V OCV and 360 mW cm^{-2} output.
- The single layer cell showed a comparable performance to the three-layer cell.
- The effects of the ratio between electronic and ionic conductions are elaborated.

GRAPHICAL ABSTRACT



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ABSTRACT

A new kind of single layer fuel cell (SLFC) based on a composite material of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ (SDC)– Na_2CO_3 and $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ (SFM) is successfully fabricated and characterized. As a mixed ionic and electronic conductor, SFM provides more reaction areas than the triple phase boundary provided by a simple mixture of ionic conductor and electronic conductor. SDC– Na_2CO_3 is used to adjust the ratio of ionic and electronic conductivities. The influence of the SFM content on the electrochemical performance of the SLFC is examined. The pellet made of 30 wt.% SFM and 70 wt.% SDC– Na_2CO_3 exhibits the highest open circuit voltage of 1.05 V and output of 360 mW cm^{-2} at 750 °C. Besides, by discussing influence factors of the OCV of the cell, the reason why the SLFC can give a similar OCV and output comparing with the conventional three-layer fuel cell, has been explained in detail.

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1. Introduction

Fuel cells are electrochemical devices that directly convert chemical energy of fuels into electrical energy with high efficiency of power generation and low environmental impacts [1]. Solid oxide fuel cells (SOFCs) have received great attention for the potential of utilizing various fuels due to their high operating

temperature, which benefits the reaction kinetics [2,3]. However, the high temperature also causes the mismatch of thermal expansion as well as inter-diffusion and interaction between electrolytes and electrodes, bringing serious mechanical and chemical problems [4–6]. Considerable efforts have been devoted to solve these problems, e.g. adding an interlayer between the electrolyte and the electrode [7–10], which would increase the complexity and the fabricating cost at the same time.

Recently, a single layer fuel cell (SLFC) was developed [11–14], and showed reasonable performance [15,16]. The fuel cell function is realized with one homogeneous layer based on a composite of

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ionic and electronic conductors. Comparing to the conventional three-layer configuration, SLFC avoids the mechanical and chemical incompatibility between electrolytes and electrodes, and provides technical advantages of simplified fabrication, stack-design and operating requirements.

The basics and fundamental issues of SLFC, such as material choice, structure and morphology, reaction activity as well as working principle, have been intensively investigated [11–14,17]. In addition, Xia et al. [18] measured the overall conductivity of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ (SDC)– $\text{Li}_{0.15}\text{Ni}_{0.45}\text{Zn}_{0.4}\text{O}_x$ in air by adjusting the relative weight percentage of the ionic conductor and electronic semiconductor. Fan et al. [19] optimized the electrochemical performance of the SLFC by adjusting the ratio of ionic and electronic conductors as well as the pellet thickness. Liu et al. [20] developed a model to simulate the distribution of gases in the porous structure of a SLFC, and revealed that the electrode reaction depth of H_2 or O_2 was 1–2 orders of magnitude smaller than the thickness of a typical pellet, which was consistent with experimental results.

As the SLFC was occasionally discovered when testing a composite electrode material of conventional three-component fuel cell [15], the materials of SLFC tested up to now are mainly mixtures of an ionic conductor, e.g. doped ceria-carbonate composite materials (SDC– Na_2CO_3), and a semiconductor such as composite of metal oxides like NiO , CuO , ZnO and Li_2O [11–14,17–19]. Thus, the performance of SLFC has been limited by the volume of the triple phase boundary (TPB) in the electrochemical reacting region, similar to the conventional electrode materials such as Ni –yttria stabilized zirconia (YSZ), Ni –SDC anode and $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_{3-\delta}$ –YSZ cathode [2,3,21–23]. In contrast, some mixed ionic and electronic conductors (MIECs), such as $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, have been developed as electrodes in recent years, which get rid of the restriction of TPB and enhance the cell performance [21,22,24]. Among them, $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{3-\delta}$ (SFM) double-perovskite is stable in both reducing and oxidizing atmospheres, and has been utilized as both the anode and the cathode of SOFCs [25–27]. However, due to the high electronic conductivity of SFM, it is not suitable to be used as the only material for composing a SLFC. Meanwhile, the doped ceria-carbonate composite materials with a promising ionic conductivity and negligible electronic conductivity, have been widely examined as electrolytes for fuel cells operating in intermediate temperature [28–32]. In this work, SFM is mixed with SDC– Na_2CO_3 [33] to obtain balanced electronic and ionic conductivities. The effects of SFM content on the electrical conductivity of the composite and the performance of the SLFC are investigated. By discussing influence factors of the OCV of the cell, the influence of the proportion of the ionic and electronic conductivities of the composite material on the performance of the SLFC is discussed.

2. Experimental

2.1. Material preparation

SFM powder was synthesized via a citrate-EDTA complexing method [34] with stoichiometric $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (Guangfu corporation, China). The mole ratio of EDTA, citric acid and total metal ions was 1:1.5:1. EDTA was dissolved in diluted aqueous solution of ammonia to form EDTA– $\text{NH}_3\cdot\text{H}_2\text{O}$ solution, then $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ was introduced under heating and stirring. $\text{Sr}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ were dissolved in deionized water and then added to the previous solution, followed by stirring and introduction of citric acid. The pH value of the final solution was adjusted to 6 using $\text{NH}_3\cdot\text{H}_2\text{O}$. The solution was then heated to 95 °C to remove excess water and to form a yellow gel. The SFM powder was prepared by slowly decomposing

the gel at 400 °C in air for 0.5 h and then calcination at 1200 °C in air for 5 h to obtain a pure double-perovskite structure.

SDC– Na_2CO_3 was synthesized by carbonate co-precipitation method as reported [35] using Sm_2O_3 and $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (Guangfu corporation, China) as starting materials. The precipitate was sintered at 800 °C for 4 h and ball milled to obtain the SDC– Na_2CO_3 powder.

The composite powders were obtained by mixing the as-prepared SFM and SDC– Na_2CO_3 powders with ratios of 10, 20, 30 and 40 wt.% SFM, respectively.

2.2. Characterization

The X-ray diffraction (XRD) patterns of the composite powders were recorded at room temperature using a D8 Focus diffractometer (Bruker Corp., Germany) with Cu–K α radiation, 40 kV and 200 mA, at a scanning rate of 10° min^{−1}. The surface morphology of the composite powder and the single cell was observed with a Hitachi S-4800 scanning electron microscope (SEM).

2.3. Conductivity test

The conductivity measurements were carried out using a DC four-probe method. Samples were pressed under 250 MPa and made into rectangular bars with a typical size of 2 × 10 × 18 mm and then calcined at 750 °C for the composite and SDC– Na_2CO_3 samples, and 1200 °C for SFM samples. Four silver wires acting as electrodes were connected to the bar with silver conductive paint. The measurements were carried out in H_2/N_2 and O_2/N_2 atmospheres, and the total gas flow rate was kept as 100 ml min^{−1} (STP). A constant direct current was supplied to the sample through the two outer wires, while the voltage drop between the two inner wires was recorded by the VERASTA2273 analyzer (Princeton Applied Research, Oak Ridge, TN, U.S.).

2.4. Fuel cell test

Composite powders were pressed under 250 MPa into pellets with a diameter of 13 mm and a thickness of 1.2 mm. For comparison, a traditional three-layer cell with the same size was also fabricated using composite with 30 wt.% SFM as electrodes material and SDC– Na_2CO_3 as the electrolyte material. For these cells, Ag paste was coated on both sides as the current collector.

Cells with the effective area of 0.64 cm² were tested from 650 to 750 °C. Hydrogen with a flow rate of 100 ml min^{−1} (STP) and oxygen with a flow rate of 30 ml min^{−1} (STP) were used as fuel and oxidant, respectively. The *I*–*V* and *I*–*P* curves of the cell were recorded using the aforementioned VERASTA2273 analyzer. Electrochemical impedance spectra (EIS) were performed in the frequency range from 1 MHz to 0.01 Hz using the same VERASTA2273 analyzer under OCV with the amplitude of 10 mV at various temperatures in both hydrogen and oxygen atmosphere.

3. Results and discussion

3.1. Structure and morphology

The XRD pattern of the composite powder shows a combination of the characteristic peaks of SFM and SDC– Na_2CO_3 , as illustrated in Fig. 1, and no other phases can be found, indicating that there is no obvious interaction between the two materials. An intensity decrease of the peaks of the SFM phase can be observed, which may be caused by the existence of the other phases. However, Na_2CO_3 phase cannot be found since it forms an amorphous shell over the SDC core [35].

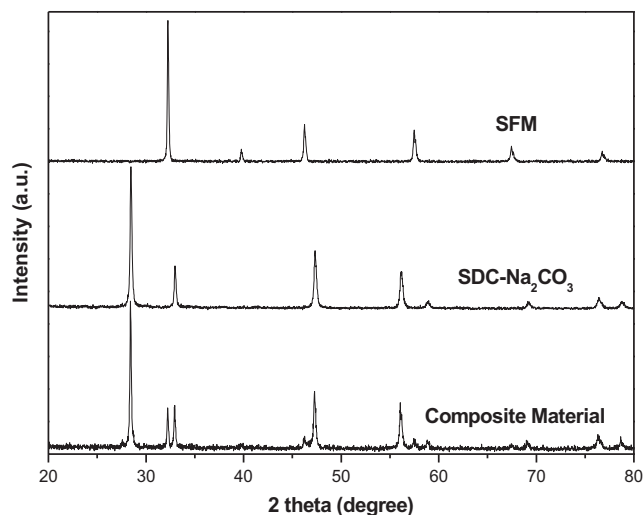


Fig. 1. XRD patterns of the as-prepared SFM, SDC–Na₂CO₃ and the composite material.

Fig. 2a shows a uniform distribution of SFM and SDC–Na₂CO₃ in the composite material, and the particle size ranges from tens up to a few hundred nanometers. Fig. 2b and c give the micrographs of the partial and whole cross-section of the SLFC after the performance measurement. SFM and SDC–Na₂CO₃ are uniformly distributed in the whole cell. Comparing to the conventional SOFC, SLFC shows a much simpler structure, and only one homogeneous layer can be seen except the current collectors. The porous structure of the whole cell would facilitate the mass transfer of reactants and products in the functional electrode region to deliver high power outputs.

3.2. DC conductivity

Table 1 gives the DC conductivity data of SFM, SDC–Na₂CO₃ and the composite with 30 wt.% SFM at 750 °C in O₂/N₂ and H₂/N₂ atmospheres, respectively. The conductivities of SFM are very dependent on the atmosphere and the preparation history. The values reported here in H₂/N₂ are much higher than those measured in O₂/N₂. This may reveal its n-type conductivity. Chen et al. [25] gave different total conductivity values as 550 S cm^{−1} in air and 310 S cm^{−1} in hydrogen, respectively. They conducted the measurement at a higher temperature, 780 °C, and the sample was sintered at 1400 °C. In another work, 0.13 S cm^{−1} in air at 800 °C for oxide ion conductivity was reported [26]. These results indicate that SFM is a mixed ionic–electronic conductor with a large portion of electronic conduction [36]. After mixing with SDC–Na₂CO₃, which is generally regarded as a pure ionic conductor [32,33,35], the 2 orders of magnitude decrease of the total conductivity, see the data in Table 1, reveals that the electronic conductivity of the composite material has been effectively reduced.

3.3. Single cell performance

For the SLFC made of only pure SFM, an OCV of 0.02 V was obtained at 750 °C. The reason is that the electronic conductivity of the pure SFM is much higher than its ionic conductivity, causing serious short circuit consequently. However, its electronic conductivity can be effectively suppressed by the addition of SDC–Na₂CO₃. As a result, the OCV of the corresponding SLFC is increased significantly, as shown in Fig. 3a. The SLFC based on 40 wt.% SFM achieves an OCV of 0.65 V at 750 °C. For the SLFC with 30 wt.% SFM, the OCV reaches 1.05 V and the maximum power density is

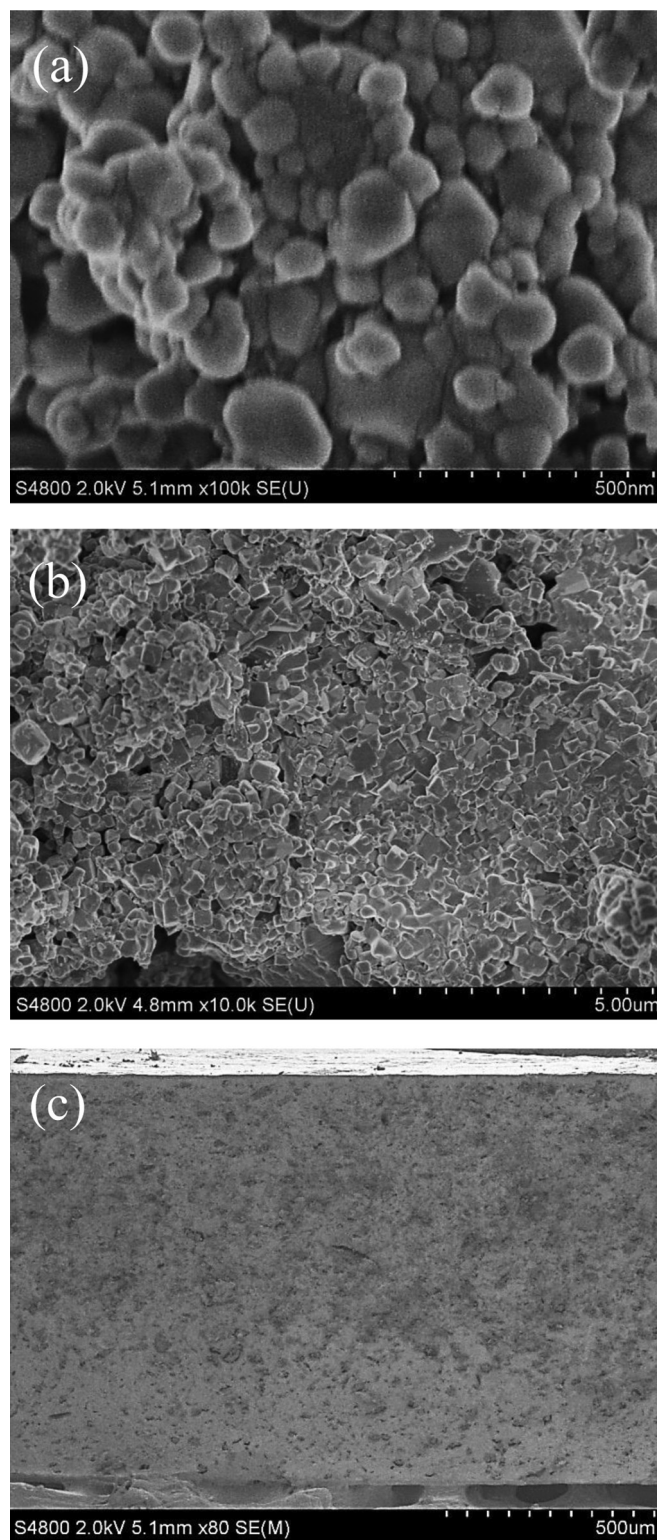


Fig. 2. SEM micrographs of (a) the composite powder; (b) the partial and (c) whole pellet cross-section of corresponding SLFC after performance measurements.

360 mW cm^{−2}. However, the OCV goes down to about 0.95 V with a further decrease of the SFM content, meanwhile the output also declines. It has been reported that an SLFC based on pure SDC–Na₂CO₃ exhibits an OCV of 0.92 V with a negligible output [19]. This is mainly caused by the lower catalytic activity of SDC–Na₂CO₃ compared to SFM. Besides, the low electronic conductivity of SDC–

Table 1DC conductivity (S cm^{-1}) of samples in (a) O_2/N_2 and (b) H_2/N_2 atmospheres at 750°C .

	100	80	60	40	20
(a) O_2 %					
Composite with 30 wt.% SFM	2.96×10^{-2}	2.92×10^{-2}	2.89×10^{-2}	2.85×10^{-2}	2.79×10^{-2}
SDC– Na_2CO_3	4.64×10^{-3}	4.78×10^{-3}	4.77×10^{-3}	4.73×10^{-3}	4.73×10^{-3}
SFM	4.94	4.79	4.62	4.41	4.03
(b) H_2 %					
Composite of 30 wt.% SFM	5.98×10^{-1}	4.69×10^{-1}	4.64×10^{-1}	4.45×10^{-1}	4.20×10^{-1}
SDC– Na_2CO_3	4.19×10^{-2}	3.86×10^{-2}	3.49×10^{-2}	3.19×10^{-2}	2.83×10^{-2}
SFM	41.1	38.0	37.0	35.6	32.8

Na_2CO_3 results in a small TPB area, which leads to a high electrode polarization. Furthermore, the EIS results in Fig. 3b indicate the ohmic resistance of the pellet reduces from 1.22Ω to 0.55Ω with the increase of SFM content due to the improvement of electronic conduction. Therefore, a balance between ionic and electronic conductivities is required for the SLFC material to achieve a promising OCV and performance.

Fig. 4a displays the I – V and I – P characteristics of the SLFC composed of 30 wt.% SFM at 650 , 700 , and 750°C , respectively. As the temperature increases from 650 to 750°C , the maximum power output is greatly enhanced from about 150 to 360 mW cm^{-2} . Meanwhile, the ohmic resistance decreases from 1.12Ω to 0.68Ω

with the elevated temperature as shown Fig. 4b. With the increase of the operating temperature, the ionic conductivities of SFM and SDC– Na_2CO_3 both increase [25,33], as well as the electronic conductivity of SFM increases [26]. However, the OCV at all temperatures is around 1.0 V , which is close to the theoretical value. As the temperature increases, the OCV rises slightly. This is probably caused by the enhancement of the electronic and ionic conductivities, and the catalytic activity of the functional electrodes. Meanwhile, the ohmic loss in the electrolyte functional region decreases due to the increased ionic conductivity, resulting in the improvement of the cell performance.

Compared to the conventional three-layered configuration with 30 wt.% SFM composite as the electrodes and SDC– Na_2CO_3 as the electrolyte, as shown in Fig. 5, the SLFC exhibits similar or even better performance. These results demonstrate that the SLFC has equivalent function as traditional three-component devices [13,14]. Both the H_2 and O_2 contacting sides satisfactorily act as the functional anode and cathode, respectively. Meanwhile, an efficient ionic conductivity is achieved in the functional electrolyte layer. Afterward, H_2 and O_2 are exchanged to the opposite sides of each other, and the cell gives an opposite number of OCV and a similar performance. This phenomenon was also observed in literature [12,14]. These results indicate that each side of the SLFC functions as an anode for hydrogen oxidation or a cathode for oxygen reduction.

4. Discussion

The electronic conduction brings positive and negative effects on the performance of the SLFCs simultaneously. With a sufficient electronic conductivity, the TPB of both anode and cathode functional regions are significantly extended, and the electrode polarizations are decreased accordingly. However, the short circuit through the electrolyte functional region results in the decrease of OCV and energy efficiency. Meanwhile, the porosity of samples would also affect the OCV by gas leakage according to Nernst equation. Then the OCV observed of an SLFC can be expressed as

$$\text{OCV} = E_0 - E_l - E_s - E_e \quad (1)$$

where E_0 represents the theoretical electromotive force of the SLFC, E_l the potential loss caused by gas leakage, E_s the potential losses of short circuit caused by the electronic conductivity of composite material, and E_e the electrode polarization affected by activity and amount of active sites, respectively.

As shown in Fig. 3a, the SLFC made of 30 wt.% SFM gives an OCV of 1.05 V and an output of 360 mW cm^{-2} at 750°C . The OCV is similar to the theoretical potential value of a H_2 – O_2 fuel cell at this temperature (around 1.0 V), which indicates that both of E_l and E_s are negligible. It has been demonstrated that the electronic conductivity of the SLFC reduces with the decrease of the SFM content.

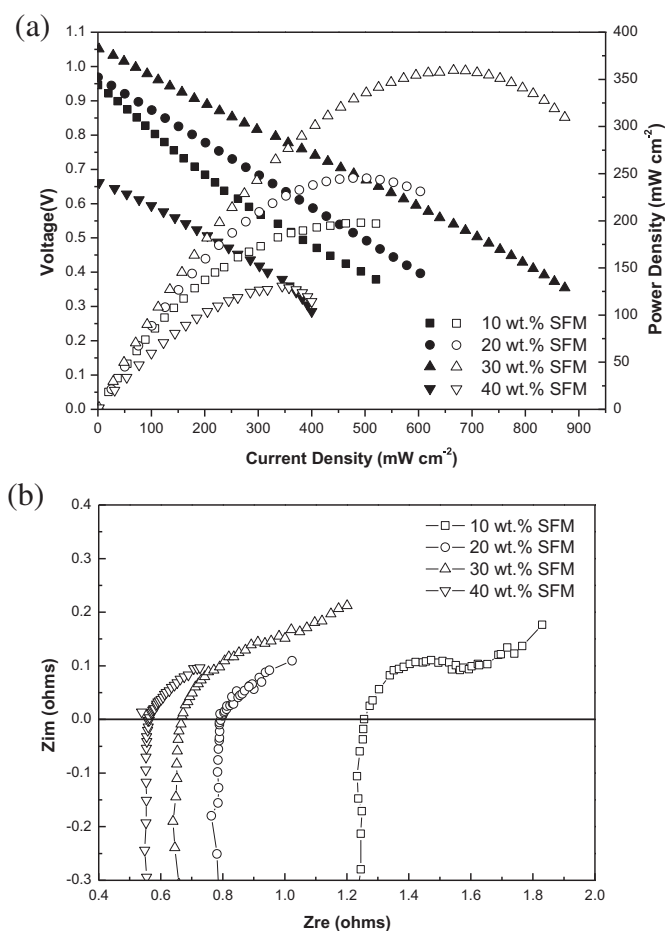


Fig. 3. Comparison of (a) I – V and I – P characteristics, (b) EIS, for SLFCs with various composition at 750°C .

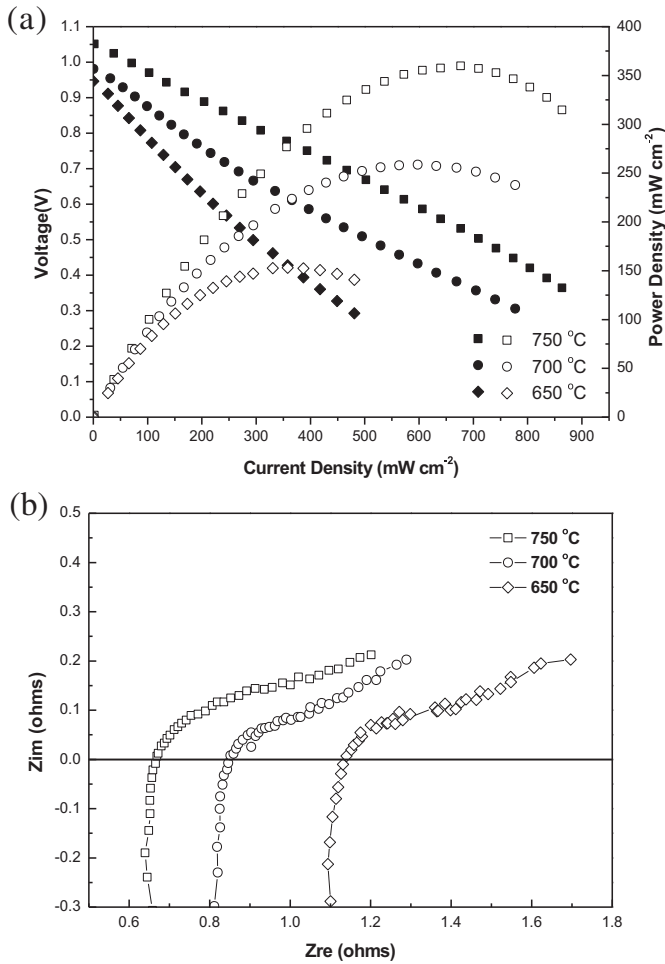


Fig. 4. (a) I - V and I - P characteristics, (b) EIS, for SLFC with 30 wt.% SFM at various temperatures.

Therefore, the E_s for SLFC with 10 wt.% SFM and 20 wt.% SFM could also be neglected. However, as the amount of SFM decreases, the active sites in anode and cathode functional regions are reduced, as mentioned previously, leading to a slightly increased E_e and OCV of 0.95 V. In contrast, the E_e of the SLFC with 40 wt.% SFM is less than

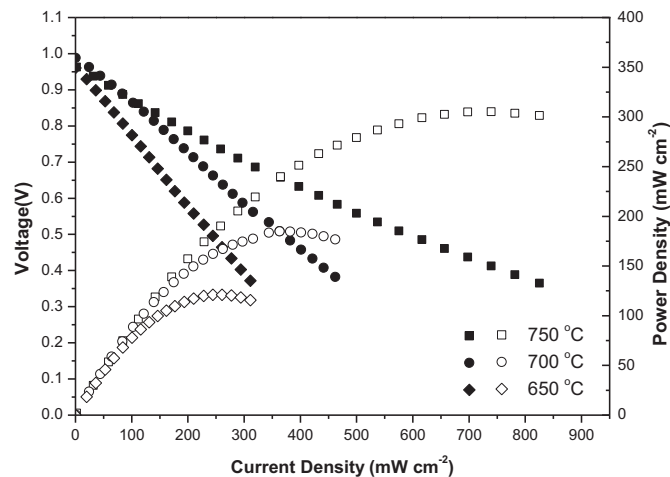


Fig. 5. I - V and I - P characteristics of the corresponding three-layer fuel cell.

that of the one with 30 wt.% SFM. However, the increased electronic conductivity results in a significantly enhanced E_s , resulting in the observed OCV of only 0.65 V. The influence of SFM content on E_e can also be investigated based on the EIS results, as illustrated in Fig. 3b. The intercept on the Z_{re} axis, which indicates the ohmic resistance of the pellet, reduces with the increase of SFM ratio due to the improvement of electronic conduction. All the Nyquist plots of SLFCs above the Z_{re} axis are consisted of a small arc followed by a “tail”. The arc is much easier to be observed from 10 wt.% SFM sample, while samples of higher SFM contents with smaller arcs suggest a decrease of reacting resistance. SFM with its mixed conduction enlarge the reaction phase of pellets which benefits the electrode reactions.

As discussed above, the E_i of SLFC with 30 wt.% SFM should be neglected at 750 °C. But the gas leakage would aggravate with the rise of operating temperature, resulting in an increase of E_i . However, the reacting activity is enhanced simultaneously, leading to a lower E_e . Overall, the OCV shows a positive correlation with the temperature, as shown in Fig. 4a. Besides, from the EIS characteristics in Fig. 4b, it is clear that with the elevated temperature, the total conductivity, and the electrode polarization decreases as the arc diminishes.

The discussion above declares that effects of short circuit and electrode polarization on OCV are much greater than that of gas leakage. And at a higher temperature, the short circuit potential loss dominates. Thus, following discussion would mainly focus on the effect of mixed ionic–electronic conduction in SLFC on its OCV and output by short circuit. E_i and E_e would have no direct correlation with conductivity. Therefore, assuming the sum of E_i and E_e is 0.05 V, and the E_0 is 1.10 V, a fuel cell with mixed ionic and electronic conduction along with the external circuit could be illustrated as Fig. 6a, where E represents E_0 subtracted by E_i and E_e of the SLFC, r_i the resistance of ionic conduction in the electrolyte, r_e and R_e the resistances of electronic conduction in the electrolyte and the external circuit, respectively. Then the OCV of SLFC could be expressed as

$$OCV = \frac{E}{1 + \beta} \quad (2)$$

where β is the ratio between the ionic and the electronic resistances of SLFC.

$$\beta = \frac{r_i}{r_e} \quad (3)$$

The output power density of SLFC on the external resistance, P , could be calculated as

$$P = \frac{R_e r_e^2 E^2}{[R_e r_e + r_i (R_e + r_e)]^2} \quad (4)$$

Equation (3) can be simplified, and when

$$R_e = \frac{1}{1 + \beta} r_i \quad (5)$$

P achieves the maximum,

$$P_{\max} = \frac{E^2}{4(1 + \beta)^2 r} \quad (6)$$

where r is the inner resistance of SLFC as r_i and r_e in parallel,

$$r = \frac{r_i r_e}{r_i + r_e} \quad (7)$$

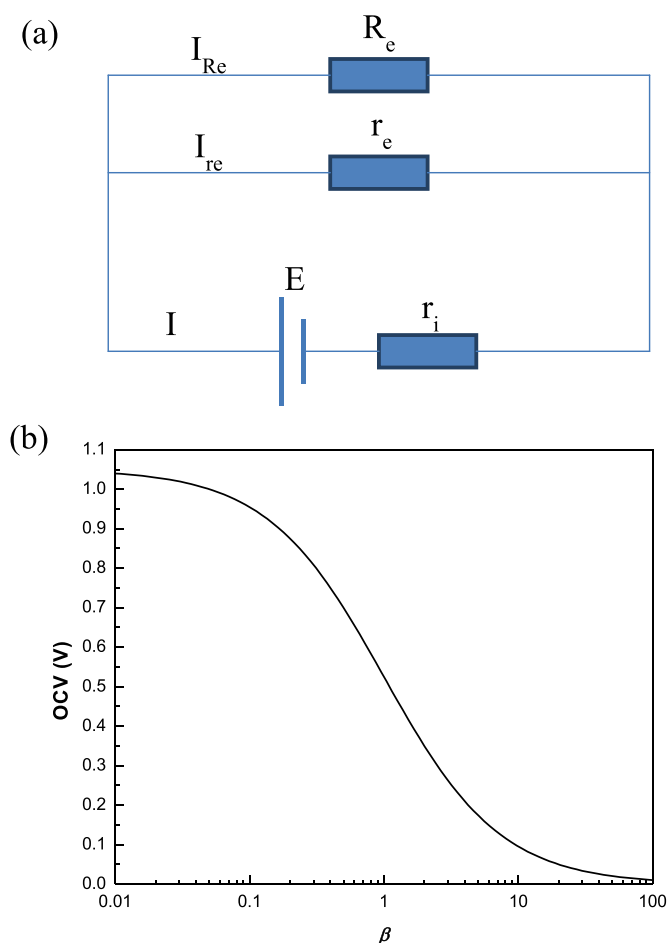


Fig. 6. (a) Schematic diagram and (b) relationship between β and OCV of SLFC with mixed ionic and electronic conduction.

Thus, the OCV of SLFC, along with the maximum power density on the external resistance, is influenced by β , which could also be explained as the ratio between electronic and ionic conductivities of SLFC. From the relationship between β and OCV as shown in Fig. 6b, the SLFC can achieve an OCV as high as about 0.95 V when β is 0.1. Therefore, by choosing a proper balance between the electronic and ionic conductivities, the OCV and output of the fuel cells prepared by mix-conductive materials in a single layer structure could be comparable to those of traditional three-layer fuel cells.

It should be noticed that some energy is wasted inside the SLFC due to the short circuit, causing the decrease of the total efficiency. However, by further optimizing the material with higher ionic conductivity to achieve proper ratio between electronic and ionic conductivities, the proportion of this waste could be minimized. Traditional SOFCs working in the 500–700 °C range usually need dual electrolyte layers to prevent electronic conduction (e.g. SOFCs with doped ceria electrolyte [21,22]) or an interlayer to prevent the interaction between electrodes and electrolyte (e.g. SOFCs with Ni anode and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{3-\delta}$ electrolyte [5,6]), which decreases the output and energy efficiency as well. Compared to the three-layer configuration, the SLFC with only one layer avoids chemical and thermal incompatibility between different components, accordingly simplifies the fabricating technology and enhances the working stability, making it a promising energy conversion device in future application.

5. Conclusion

A new kind of single layer fuel cell composed of SFM and SDC– Na_2CO_3 was fabricated and characterized. The composition of the material exerts significant influence on the SLFC performance. The SLFC made of 30 wt.% SFM and 70 wt.% SDC– Na_2CO_3 exhibits the highest OCV of 1.05 V and output of 360 mW cm^{-2} at 750 °C. The good performance and the low electrode polarizations are attributed to the proper balance of the electronic and ionic conductivities of the material.

By discussing influence factors of the OCV of the cell, the effects of mixed ionic–electronic conduction in SLFC on its OCV and output have been revealed, which indicates the possibility for fuel cells prepared by mixed conduction material in single layer structure to provide comparable OCV and output to conventional three-layer fuel cells. Therefore, if SLFC can be prepared by one single material which has balanced ionic and electronic conduction simultaneously in both reducing and oxidizing atmospheres, further simplification of fuel cell without the limitation of TPB can be realized to promote the progress of future marketable fuel cells.

Acknowledgments

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References

- [1] B.C.H. Steele, A. Heinzel, *Nature* 414 (2001) 345–352.
- [2] S. McIntosh, R.J. Gorte, *Chem. Rev.* 104 (2004) 4845–4865.
- [3] R.J. Gorte, J.M. Vohs, in: J.M. Prausnitz (Ed.), *Annual Review of Chemical and Biomolecular Engineering*, vol. 2, 2011, pp. 9–30.
- [4] F. Tietz, *Ionics* 5 (1999) 129–139.
- [5] P. Huang, A. Horky, A. Petric, *J. Am. Ceram. Soc.* 82 (1999) 2402–2406.
- [6] K.N. Kim, B.K. Kim, J.W. Son, J. Kim, H.W. Lee, J.H. Lee, J. Moon, *Solid State Ionics* 177 (2006) 2155–2158.
- [7] Z. Bi, B. Yi, Z. Wang, Y. Dong, H. Wu, Y. She, M. Cheng, *Electrochem. Solid-State Lett.* 7 (2004) A105–A107.
- [8] J. Yan, H. Matsumoto, M. Enoki, T. Ishihara, *Electrochem. Solid-State Lett.* 8 (2005) A389–A391.
- [9] Y. Lin, S.A. Barnett, *Electrochem. Solid-State Lett.* 9 (2006) A285–A288.
- [10] W. Guo, J. Liu, Y. Zhang, *Electrochim. Acta* 53 (2008) 4420–4427.
- [11] B. Zhu, Y. Ma, X. Wang, R. Raza, H. Qin, L. Fan, *Electrochem. Commun.* 13 (2011) 225–227.
- [12] B. Zhu, H. Qin, R. Raza, Q. Liu, L. Fan, J. Patakangas, P. Lund, *Int. J. Hydrogen Energy* 36 (2011) 8536–8541.
- [13] B. Zhu, R. Raza, G. Abbas, M. Singh, *Adv. Funct. Mater.* 21 (2011) 2465–2469.
- [14] B. Zhu, R. Raza, H. Qin, L. Fan, *J. Power Sources* 196 (2011) 6362–6365.
- [15] L. Fan, C. Wang, M. Chen, B. Zhu, *J. Power Sources* 234 (2013) 154–174.
- [16] B. Zhu, L. Fan, P. Lund, *Appl. Energy* 106 (2013) 163–175.
- [17] B. Zhu, R. Raza, Q. Liu, H. Qin, Z. Zhu, L. Fan, M. Singh, P. Lund, *RSC Adv.* 2 (2012) 5066–5070.
- [18] Y. Xia, X. Liu, Y. Bai, H. Li, X. Deng, X. Niu, X. Wu, D. Zhou, M. Lv, Z. Wang, *J. Meng, RSC Adv.* 2 (2012) 3828–3834.
- [19] L. Fan, C. Wang, O. Osamudiamen, R. Raza, M. Singh, B. Zhu, *J. Power Sources* 217 (2012) 164–169.
- [20] Q. Liu, H. Qin, R. Raza, L. Fan, Y. Li, B. Zhu, *RSC Adv.* 2 (2012) 8036–8040.
- [21] A.J. Jacobson, *Chem. Mater.* 22 (2010) 660–674.
- [22] A. Aguadero, L. Fawcett, S. Taub, R. Woolley, K.-T. Wu, N. Xu, J.A. Kilner, S.J. Skinner, *J. Mater. Sci.* 47 (2012) 3925–3948.
- [23] P.I. Cowin, C.T.G. Petit, R. Lan, J.T.S. Irvine, S. Tao, *Adv. Energy Mater.* 1 (2011) 314–332.
- [24] Y.-H. Huang, R.I. Dass, Z.-L. Xing, J.B. Goodenough, *Science* 312 (2006) 254–257.
- [25] Q. Liu, X. Dong, G. Xiao, F. Zhao, F. Chen, *Adv. Mater.* 22 (2010) 5478–5482.
- [26] G. Xiao, Q. Liu, F. Zhao, L. Zhang, C. Xia, F. Chen, *J. Electrochem. Soc.* 158 (2011) B455–B460.
- [27] H. Li, Y. Tian, Z. Wang, F. Qie, Y. Li, *RSC Adv.* 2 (2012) 3857–3863.
- [28] C. Xia, L. Li, Y. Tian, Q.H. Liu, Y.C. Zhao, L.J. Jia, Y.D. Li, *J. Power Sources* 188 (2009) 156–162.

- [29] C. Xia, Y. Li, Y. Tian, Q.H. Liu, Z.M. Wang, L.J. Jia, Y.C. Zhao, Y.D. Li, J. Power Sources 195 (2010) 3149–3154.
- [30] Y.C. Zhao, C. Xia, Y.J. Wang, Z.R. Xu, Y.D. Li, Int. J. Hydrogen Energy 37 (2012) 8556–8561.
- [31] Y.C. Zhao, C. Xia, Z.R. Xu, Y.D. Li, Int. J. Hydrogen Energy 37 (2012) 11378–11382.
- [32] Y. Zhao, Z. Xu, C. Xia, Y. Li, Int. J. Hydrogen Energy 38 (2013) 1553–1559.
- [33] X. Wang, Y. Ma, S. Li, A.-H. Kashyout, B. Zhu, M. Muhammed, J. Power Sources 196 (2011) 2754–2758.
- [34] Z. Wang, Y. Tian, Y. Li, J. Power Sources 196 (2011) 6104–6109.
- [35] R. Raza, X. Wang, Y. Ma, X. Liu, B. Zhu, Int. J. Hydrogen Energy 35 (2010) 2684–2688.
- [36] J. Richter, P. Holtappels, T. Graule, T. Nakamura, L.J. Gauckler, Monatsh. Chem. 140 (2009) 985–999.